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MESH-LIKE POROUS HOLLOW YARN MEMBRANE
[AMIMEJOU TAKOUSHITSU CHUUKUU ITO MAKU]

YOSHIAKI NITORI et al.

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INVENTOR(S)	(72):	Yoshiaki Nitori Takeaki Hagiwara
APPLICANT(S)	(71):	Asahi Medical Co.
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FOREIGN TITLE	[54A]:	Amimejo Takousitsu Chuukuu Ito Maku

Specification

1. Title of Invention

Mesh-Like Porous Hollow Fiber Membrane

2. Scope of Claims

(1) A mesh-like porous hollow fiber membrane having a cellular structure formed from microfibril bundles in which a plurality of microfibrils oriented in the fiber axial direction are bundled by a linear polymer, and knotted portions comprising stacked lamella intersecting with and bonding to both ends of said bundles; said hollow fiber membrane characterized by the microfibrils and stacked lamella comprising a crystalline polymer covered by a linear polymer, and further, said membrane forming a substantially uniform three-dimensional mesh structure overall, and the spatial parts thereof forming elliptical through-holes oriented in the fiber axial direction.

(2) The hollow fiber membrane of Claim 1 wherein the average interval ($\overline{\ell} s$) μm between stacked lamella, the average interval ($\overline{\ell} s$) μm of the microfibril bundles, and the ratio of these having the relationship:

$$0.2 \leqq \overline{\ell} s \leqq 5 \quad (\mu m)$$

$$0.1 \leqq \overline{d} b \leqq 3 \quad (\mu m)$$

$$1 \leqq \overline{\ell} s / \overline{d} b \leqq 5$$

(3) The hollow fiber membrane of Claim 2 wherein the average interval $(\bar{d}bi)$ μm of the microfibril bundles on an interior surface portion, the average interval $(\bar{d}bo)$ μm of the microfibril bundles on an exterior surface portion, and the average interval μm of the microfibril bundles in the center portion perpendicular to the membrane having the relationship:

$$0.8 \leq \bar{d}bc / \bar{d}bi \leq 1.2$$

$$0.8 \leq \bar{d}bc / \bar{d}bo \leq 1.2$$

(4) The hollow fiber membrane of any one of Claims 1 to 3 wherein the maximum hole diameter of the elliptical through-hole found in a bubble point method is 0.1 to 1.0 μm.

(5) The hollow fiber membrane of any one of Claims 1 to 4 wherein the crystalline polymer is a polyolefin.

(6) The hollow fiber membrane of Claim 5 wherein the

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polyolefin is polyethylene or polypropylene.

(7) The hollow fiber membrane of any one of Claims 1 to 6 wherein the linear polymer is an olefin copolymer.

(8) The hollow fiber membrane of Claim 7 wherein the olefin copolymer is an ethylene/vinyl alcohol copolymer.

3. Detailed Description of the Invention

(Field of Industrial Application)

The present invention relates to a porous hollow fiber membrane having improved solute permeability.

(Prior Art)

Porous membranes using a polymer compound as the raw material are utilized widely in the filtering of water-based solutions or water-based suspensions. In the industrial field, porous membranes are used for manufacturing purified water for the electronic industry and the like, sterilizing raw water for manufacturing pharmaceuticals, battery separators, and the like, and in the medical field, for separation of blood components, removal of [illegible] shaped components during dessication, removal of foreign bodies during various transfusions, for various sterilization filers, etc.

For example, techniques for separating blood into various components by membrane separation method have been put to practical use in the medical field, and of these, plasma separation membranes, which separate blood into blood cell components and plasma components, had begun to be used for many medical purposes, such as plasma pheresis, in which the plasma of a patient having etiological components in his/her plasma was separated and discarded, then replenished with the plasma of a healthy person; plasma cleansing treatments, in which the plasma is separated, subsequently cleaned and returned to the patient; plasma collection for collecting only plasma from healthy persons; and further, separation of banked plasma or the like, where banked blood is separated into blood cell components and plasma components.

For methods for manufacturing the porous membrane comprising the polymer compound, there are, among others, wet film formation methods; melt phase transition methods, in which additives, such as plasticizer, are mixed, melted, and molded, and the additives are subsequently extracted and removed; and drawing perforation methods, which are used in the case of crystalline polymers.

In a drawing perforation method, a crystalline polymer is melted and molded, the crystal lamella are subsequently cleaved by cold-drawing, and enlargement of pores is then performed by a hot-drawing, after which the structure is fixed by thermosetting. The pores are formed from microcapsules elliptically-oriented in the drawing direction and knotted portions comprising stacked lamella communicating with these microcapsules. As for the structure of the pores thereof, a base unit of the strip-shaped structure is laminated one on another to form pores on both sides communicating with one another through the membrane. Since additives, such as organic solvents or plasticizers, are not added to the porous membrane obtained in this method during the manufacturing process, an additive extraction operation is unnecessary. Moreover, there is no concern that any residual additives will elute out during use, and it is useful as a highly safe porous membrane even for use in medical applications. Porous hollow fiber membranes, in which a high-density polyethylene was perforated in a drawing perforation method, were proposed as examples thereof (Japanese Unexamined Patent Application Publication Nos. S52-137026, S57-42919, S57-66114 and S57-84702).

(Problems to be Solved by the Invention)

For the purpose of separating formed components and liquid components in aqueous systems and various solvent systems, it is necessary that porous membranes for separation have high passing rates, sufficient permeation ability for liquid components but obstruction of formed components, sufficient strength, etc.

In particular, when porous membranes are used for plasma separation films, the following functions and characteristics are demanded.

(1) That blood cell components be obstructed but that the target plasma components be allowed to completely pass through.

(2) That it be small and the plasma separation performance be high.

(3) That it be highly safe.

Item (1) will be described in detail. The target components allowed to pass through vary somewhat depending on the purpose for performing the plasma separation. With plasma separation for the purpose of medical treatment, immunoglobulins, immunocomplexes, low-density lipoproteins (LDLs), and the like are cited as substances to be removed. Such substances to be removed are generally high molecular weight substances, and the molecular size thereof is also large. For example, the molecular weight of an immunoglobulin, IgM, is 900,000 and its molecular size is 350Å. While immunocomplexes are not specific substances, their molecular weights are assumed to be from one million to several million, and their molecular sizes range from about 200 Å to 500Å.

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In addition, an LDL is a macromolecule having a molecular weight of 2,200,000 to 3,500,000 and a molecular size of 200 to 300Å.

In the separation of plasma for plasma collection purposes, namely, for the purpose of collecting useful plasma components, besides relatively low molecular weight components, such as albumin (molecular weight: 60,000, molecular size: 40Å×150Å), there are also high molecular weight components, such as immunoglobulins and fibrinogens (molecular weight: 34,000, molecular size: 30Å×700Å), and further, there are components whose molecular weights range from 1,000,000 to 2,000,000 or more, such as blood-coagulating factor VIII, which is used for treating hemophilia. Plasma components that are also allowed to pass through for both medical treatment and plasma collection, even for the purpose in either the treatments or plasma collection as such, are macromolecules having a molecular size on the order of several hundred Å.

In relation to the porous membrane in (2) above, the following two requirements are desired.:

(a) That components can be separated in as short a time as possible, and

(b) that the extracorporeal blood volume be as small as possible. A hollow fiber-type plasma separation membrane has advantages in that miniaturization thereof is more possible and the priming volume is smaller than that of a flat membrane. But it would be extremely useful if a membrane having a higher passing rate could be realized, and further, if miniaturization were possible, and moreover, the separation time could be reduced.

Since additives, organic solvents and the like were not used in the manufacturing process of conventionally-known hollow fiber-type porous membranes comprising polyethylene, which were obtained in a drawing perforation method, they had superior features, among others, because they were free of the problems of eluates and the like, their strength in water-based liquids was high, they were inactive in living bodies and did not adversely affect blood. However, the molecular sizes for fractionation and the passing rates of polyethylene hollow fiber-type porous membranes disclosed in prior art are insufficient for practical plasma separation membranes. Even in the Working Example 4, in which the highest performance out of the working examples disclosed in Japanese Unexamined Patent Application Publication No. S57-84702 is shown, although a passing rate of purified water of 4.6 L/hr-m^2-mmHg, a human serum albumin permeability of 98%, a total protein permeability of 90%, and a high protein permeability are shown, the low total protein permeability of 90% shows that the molecular size for fractionation is small and that the passing rate is also a low value. In addition, in the Working Example 1 disclosed in Japanese Unexamined Patent Application Publication No. S57-66114, despite the average pore size of the pores measured with a mercury porosimeter being extremely large at 0.82 µm, the water permeation volume was low at 3,200 L/hr-m^2-760 mmHg (4.2 L/hr-m^2-mmHg), and further, the permeability of Blue Dextran having a molecular weight of 2,000,000 was extremely low at 50%.

The structure of a hollow fiber-type porous membrane produced in a drawing perforation method adopts a mesh-like structure formed from numerous microcapsules oriented in the drawing direction and knotted portions comprising stacked lamella communicating at a nearly right angle to these microcapsules. But since the pores are formed from microfibrils oriented in the drawing direction, they are elliptical strip-shaped holes extending in the fiber axial direction, and the ratio of the vertical and horizontal lengths of the pores thereof amounts to 10-fold or greater. When the penetration of particles through these pores was considered, the penetrability was determined by the breadth of these pores. But whereas the pore length could be easily controlled by changing the draw ratio, the breadth could hardly be changed even if the draw ratio was changed, so a porous membrane having a sufficiently large breadth could not be obtained.

(Means for Solving the Problems)

In the prior art, as described above, a crystalline polymer membrane obtained in a drawing perforation method did not have a sufficient penetrable pore size so the penetrability to high molecular weight plasma components was insufficient for a membrane for plasma separation use.

As a result of performing meticulous research to solve the above problems, the inventors of the present invention completed the present invention. That is, the present invention relates to a porous hollow fiber membrane comprising a crystalline polymer with an improved penetration function produced by making use of drawing principles.

The porous hollow fiber membrane of the present invention is a mesh-like porous hollow fiber membrane having a cellular structure formed from microfibril bundles in which a plurality of microfibrils oriented in the fiber axial direction are bundled by a linear polymer, and knotted portions comprising stacked lamella intersecting with and bonding to both ends of said bundles; said hollow fiber membrane characterized by the

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microfibrils and stacked lamella comprising a crystalline polymer covered by a linear polymer, and further, said membrane forming a substantially uniform three-dimensional mesh structure overall, and the spatial parts thereof forming elliptical through-holes oriented in the fiber axial direction.

The sufficient penetrability of high molecular weight components, which was a problem according to prior art, was improved substantially according to the present invention, and moreover, a porous hollow fiber membrane completely free of the problems in terms of safety when used as a plasma separation membrane could be obtained.

(Effects and Embodiments)

The porous hollow fiber membrane of the present invention is a mesh-like porous hollow fiber membrane comprised by bundling, with a 2nd polymer, and completely covering the entire surface of plurality of bundles of microfibrils of a porous hollow fiber membrane precursor comprising a crystalline polymer produced by using conventionally-known drawing perforation principles. The term "bundle the microfibrils with a 2nd polymer" herein means a bundle which does not return to the precursor state prior to bundling due to dissociation once a plurality of microfibrils are bundled with the 2nd polymer.

The numerous extremely fine microfibrils in the porous hollow fiber membrane precursor obtained in the drawing perforation method of the prior art are oriented in the fiber axial direction to form parallel strip-shaped holes. But in the porous film of the present invention, the plurality of microfibrils are bundled with the 2nd polymer, whereby drum-shape columnar microfibril bundles whose middle was covered are formed. The microfibril bundles and the stacked lamella surface are simultaneously covered by the 2nd polymer. As a result, the pores formed by the above-mentioned microfibril bundles and stacked lamella are elliptical pores oriented in the fiber axial direction having an elliptical length nearly identical to the pore length of the strip-shaped pores of the above-mentioned precursor of the porous hollow fiber membrane and having a strip-shaped length over several times the pore width of the strip-shaped pores. Although the penetrability of the particles through the pores is generally determined by the size of the particles and the pore size, in the case of strip-shaped or elliptical pores, it is determined by the minor axis thereof. The minor axis of the elliptical pores is larger than the known breadth of the strip-shaped holes; hence, the particle penetrability is greatly improved.

In addition, the surfaces of the microfibril bundles and the stacked lamella are covered by the 2nd polymer; hence, the ends of the surface are round, so there is a merit in that it is difficult to damage blood cells when the membrane is used for blood plasma treatments, etc.

Moreover, the cellular structure formed by the microfibril bunds and the stacked lamella is oriented in the fiber axial direction, and is distributed evenly three-dimensionally—in the direction perpendicular to the membrane, in the circumferential direction and in the fiber axial direction; hence, the overall membrane can contribute to permeation and exhibits a high permeation rate. In addition, the membrane overall has a uniform porosity; hence, it has excellent mechanical strength.

The penetration efficiency for substances is high with the mesh-like porous membrane of the present invention; hence, it exhibits a sufficient penetration performance even when the draw ratio and porosity are increased more than necessary. Therefore, the elliptical length of the pores formed on the inner surface is kept low, and it may impede hemolysis during filtering of blood.

It can be confirmed that the cellular structure of the porous membrane of the present invention is distributed uniformly in a three-dimensional manner by observation under an electron microscope. In all of the photographs of the inner surface, outer surface and cross section in the perpendicular direction to the membrane, an image is produced in which the cellular structure is formed from microfibril bundles and knotted portions comprising stacked lamella substantially orthogonal on average and bonded to both ends of the microfibril bundles was distributed evenly.

The uniformity of the distribution in the electron micrographs can be evaluated by comparing the outer surface portion of the membrane, the center portion in the direction perpendicular to the membrane, and the inner surface of the membrane. In particular, a transmission electron micrograph of an excised membrane slice produces a satisfactory two-dimensional image; hence, quantitation by image processing is possible. It is preferable that the average interval $\overline{d}bi$ μm of the microfibril bundles in the inner surface portion, the average interval $\overline{d}bo$ μm of the microfibril bundles on the outer surface portion, and the average interval $\overline{d}bc$ on the inner surface portion found in this method have the relationships:

$$0.8 \leq \overline{d}bc / \overline{d}bi \leq 1.2$$

$$0.8 \leq \overline{d}bc / \overline{d}bo \leq 1.2$$

In addition, as for the size of the elliptical pores of the porous membrane of the present invention, the length is found as an interval between stacked lamella in the longitudinal direction of the fibers, the width is found as an interval between microfibril bundles, and the ellipticity is found as a ratio of both of these. But in order to show a satisfactory penetration performance, an average interval $\bar{l}_s$ μm between stacked lamella, an average interval $\bar{d}_b$ μm of the microfibril bundles, and the ratio of these preferably have the relationships:

$$0.2 \le \bar{l}_s \le 5 \quad (\mu m)$$
$$0.1 \le \bar{d}_b \le 3 \quad (\mu m)$$
$$1 \le \bar{l}_s / \bar{d}_b \le 5$$

Furthermore, the maximum pore size of the through-holes can be found in the bubble point method shown in ASTM F316-70. But the pore size can be chosen depending on the purpose. A bubble point pore size of 0.1 to 1.0 μ is preferable for the purpose of plasma separation.

Although the filtering rate of a liquid is found from the permeation rate of water, the higher the water permeation rate, the more preferable it is, and 1 to 30 L/hr-m^2-mmHg is preferable.

The crystalline polymer used in the present invention is a polymer having crystallinity to the extent that the principles of a drawing perforation method can be applied. Specifically, it is a polymer having a crystallinity of at least 20% or more, and preferably, 50% or more, depending on the shape of the film or hollow fibers.

Polyolefins, such as polyethylene, polypropylene, and poly-4-methyl pentane-1; polyoxymethylene or random or block copolymers in which one part is substituted with an oxyethylene chain; aromatic polyesters, such as polyvinylidene fluoride, polytetrafluoroethylene, polyphenylene oxide, polyphenylene sulfide, polyethylene terephthalate, and polybutylene terephthalate; polyamides, such as nylon 6, nylon 66, and nylon 12; and so forth are cited as typical examples of the crystalline polymer of the present invention. However, polyethylene and polypropylene are preferable because their crystallinity is high and they are suitable for a drawing perforation method.

The "drawing perforation method" in the present invention is a method for forming fine through-holes by drawing the molded compact comprising the crystalline polymer, for example, as disclosed in Tokuko JP-B No. S55-32531. This method is a method comprising the sequential steps of: molding the crystalline polymer into a film shape, hollow fiber shape, or the like by melt extruding it; subsequently performing an annealing treatment, as needed, to grow the crystals; causing cleavage between the crystal lamella by cold-drawing, and further, performing enlargement of the pores by hot drawing; and subsequently fixing the structure by thermosetting.

The 2nd polymer used in the bundling and covering in the present invention may be any polymer as long as it is soluble in a solvent. Various linear polymers may be used. Natural polymers, such as cellulose and derivatives thereof; synthetic polymers like condensation polymers, such as polyester, polyamide and polycarbonate; main chain heteroatom-containing polymers, such as polyethers; main chain carbon-type polymers; and the like are cited as examples of linear polymers. Of these, main chain carbon chain-type polymers are preferably used because a copolymer having diverse properties is obtained by copolymerization of a vinyl-based monomer. The "vinyl-based monomer" is a monomer having a carbon-carbon double bond. An olefin, such as ethylene or propylene; an aromatic vinyl monomer, such as styrene; a halogenated vinyl monomer, such as vinyl chloride; an acrylic monomer, such as methyl methacrylate or acrylonitrile; a vinyl ester, such as vinyl acetate; and the like are cited therefor.

When a polyolefin is used as the crystalline polymer, an olefin-based copolymer containing an olefin-based monomer unit is preferred for the linear polymer because its adhesion to the polyolefin is good. Any type of random copolymer, graft copolymer, block copolymer can also be used for the copolymer. An ethylene/vinyl acetate copolymer, ethylene/unsaturated carboxylic acid ester copolymer, ethylene/unsaturated carboxylic acid copolymer, ethylene/vinyl alcohol copolymer, and the like are cited as examples of the olefin-based copolymer.

Although the surface of the porous membrane of the present invention is covered by the above-mentioned linear polymer, when the liquid serving as the filtering control is a water-based

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liquid, such as blood, and when the porous surface is hydrophobic, this liquid cannot be filtered at normal pressure due to the surface tension of the water-based liquid. Therefore, this linear polymer preferably exhibits hydrophilicity, so an ethylene/vinyl alcohol copolymer is cited as an example thereof.

The method for manufacturing the porous membrane of the present invention is performed by using a porous hollow fiber comprising a crystalline polymer obtained in a conventionally-known drawing perforation method as a precursor. The 2nd polymer (linear polymer) is dissolved in an organic or inorganic solvent and supplied to this precursor as a solution. This solution permeates sufficiently inside the precursor, after which the solvent is gradually evaporated off, whereby the precursor microfibrils are bundled and covered by the linear polymer, and simultaneously, the precursor stacked lamella are also covered by the linear polymer. In this step, the change in the structure of the entire hollow fiber occurs in the direction in which the precursor shrinks in the longitudinal direction of the fibers. Finally, the solvent is sufficiently removed, the change in the structure is accelerated by a heat treatment, as needed, and the mesh-like porous hollow fiber membrane of the present invention is obtained.

The following conditions are cited for the preferred manufacturing conditions. If the polymer concentration in the polymer solution is too low, the bundling of the precursor microfibrils cannot be done sufficiently, and if the concentration is too high, permeation thereof into the interior of the precursor is difficult; hence, 0.1 to 5% is preferable, while 0.5 to 2% is more preferable for the concentration. The solvent is chosen from a good inorganic or organic solvent for the polymer. The method for supplying the polymer solution into the precursor includes a method in which it is supplied from the external surface of the precursor hollow fiber or a method in which it is supplied from both the internal surface and exterior surface. The latter method has a feature in that the polymer solution can permeate as far as the interior of the precursor in a relatively short amount of time, while the first method has a feature in that it can also be applied to a long, continuous hollow fiber. The time it takes to supply the polymer solution to the precursor and permeate as far as the interior of the precursor prior to drying ranges from 1 second to about 1 hour in accordance with the characteristics of the precursor and the polymer solution. The amount of the linear polymer with respect to the crystalline polymer is preferably 1 to 30% by weight, and more preferably, 5 to 20% by weight of the former.

The drying conditions are important because, in this step, the bundled microfibril bundles are formed, the structural change occurs, the pores become elliptical, and a reduction in the $\bar{\ell}_s / \bar{d}_b$ occurs. A rapid drying is not preferable because the structure becomes fixed without a sufficient structural change.

It takes preferably at least 1 minute, and more preferably, 10 or more minutes to dry the solvent gradually. In addition, preferably the higher the drying temperature, the more easily the structural change occurs, and any given temperature at or below the melting point of the crystalline polymer is chosen. As the temperature increases, the $\bar{\ell}_s$ tends to decrease and the $\bar{d}_b$ rise while being accompanied by shrinkage in the longitudinal direction of the fibers. The pore size of the through-holes also increases. It is preferable to gradually dry the solvent at a high temperature under a solvent evaporating atmosphere to repress a rapid drying of the solvent and perform a high-temperature drying.

Once the solvent is dried, the above-mentioned structural change can be subsequently quickened, as needed, by a heat treatment. In this case, any given temperature at or below the melting point of the crystalline polymer can be selected.

The mesh-like porous hollow fiber membrane of the present invention can be used for various blood separation membranes, sterilizing filters, filters for transfusion, filters for water treatments, food separation, concentration filters, and the like as well as for filters for hollow fiber-type cell incubators.

Furthermore, the present invention is described next according to working examples. Moreover, measurement of the various physical properties was performed according to the following methods.

(1) Average interval $\bar{D}_s$ between stacked lamella and average interval $\bar{d}_t$ between microfibrils

The sample was embedded in an acrylic resin, an ultrathin slice was prepared in a freeze-drying slicing method and removed, carbon was vapor deposited, and a 6,500X transmission electron micrograph was obtained (Figure 4). An image processing of this photograph was performed by using a TAS-Plus image processor made by Leitz. An image of the stacked lamella portion was obtained as the darkest region from a high-density crystal portion, and could be discriminated from an intermediate dark portion of the microfibril bundle. To measure the $\bar{L}_s$, this photograph was cut into a strip shape having a 0.057 µm width by the actual length in the longitudinal direction of the fibers, and the distance between respective stacked lamella was found to obtain the total average.

To measure the $\bar{d}_b$, the photograph was cut into a strip shape having a 0.047 µm width by the actual length in the perpendicular direction to the fiber length, and the distance between each microfibril bundle was found to obtain the total average.

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(2) Maximum bubble point pore size

Based on the principles of ASTM F316-70, the force at which bubbles were initially generated by pressurizing from the inside of the porous hollow fiber membrane with air in ethanol was found as the bubble point pressure, and the maximum bubble point pore size was obtained based on the pore size.

(3) Water permeation rate (L/hr-m^2-mmHg)

This was measured at a differential pressure of 50 mmHg at 37°C using purified water.

(4) Standard particle penetrability

As standard particles, (a) colloidal silica having a 0.08 μm average particle size ("Cataloid SI80P," made by Catalysts & Chemicals Industries Co., Ltd.), (b) a styrene/butadiene latex having a 0.20 μm particle size ("SBR 636," made by Dow Chemical Co.,), and (c) a polystyrene latex having a 0.33 μm average particle size ("Uniform Latex," made by Dow Chemical Co.,) were used.

In the measurement method, an aqueous suspension of the standard particles was prepared, filtering was performed on the solution at a differential pressure of 50 mmHg, the concentration was found by nephelometry at a 500 nm wavelength, and the penetrability (SC) (=Cf/Co)×100(%) (Cf: concentration of particles in permeating liquid; Co: concentration of particles in stock solution) was found.

(5) (Tensile strength at break (Kgf/cm^2), tensile elongation at break (%))

These were measured at a strain speed of 200%/min. using an Instron pull tester.

(Working Example 1)

A hollow fiber was spun from a high-density polyethylene (density: 0.968; MI: 5.5; trade name: Hyzex 2208) using an annular double spinneret, at an extrusion rate of 15 g/min., a spinning rate of 200 m/min., and a spinneret temperature of 150°C, and cooling was performed with 0.5 m/sec air. The resultant hollow fiber was annealed for 2 hours at 115°C, the rotating speed of the feed roll was adjusted, then a 1.33-fold cold drawing was performed at room temperature, and then a 3-stage hot drawing at 97°C in the 1st stage, 113°C in the 2nd stage, and 115°C in the 3rd stage was performed to 4.0-fold, 5.1-fold, and 5.8-fold with respect to the undrawn fiber. A precursor porous hollow fiber was performed by performing a 2-minute thermosetting at 115°C on the drawn hollow fibers. The precursor had strip-shaped pores formed by the microfibrils and stacked lamella, as shown in Figure 3. The various physical properties thereof are as shown in Table 1.

An ethylene/vinyl alcohol copolymer having a 29% by mole ethylene content (Soarnol D, made by The Nippon Synthetic Chemical Industry Co., Ltd.) was heated and dissolved in a 60 % by volume aqueous ethanol solution to obtain a 1.0% by weight solution. The temperature of this solution was maintained at 55°C, the aforesaid precursor porous hollow fiber were tied up in a bundle, immersed in this solution and set aside for 1 minute. Next, excess copolymer solution was removed after which the fibers were dried without tension for 1.5 hours using 60°C hot air.

The porous hollow fibers shrunk 95% less than the precursor according to the above-mentioned operation. The weight of the deposited ethylene/vinyl alcohol copolymer was 9.3% by weight.

Several to several tens of the microfibrils of the resultant porous hollow fiber membrane are bundled by the ethylene/vinyl alcohol copolymer, as shown in Figure 1, a drum-shaped column is formed, and elliptical pores wherein the pore width increased largely is shown. In addition, as shown in Figure 2, the inner surface portion, outer surface portion, and perpendicular cross section of the membrane each shows a uniform mesh-like structure. Excellent mechanical features including a tensile strength at break of 530 Kgf/cm^2 and a tensile elongation at break of 34% were shown. The various physical properties of the resultant mesh-like porous hollow fiber membrane have been shown in Table 1. However, excellent water permeability and standard particle penetrability were shown.

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表 1

		前駆体	多孔質膜
中空糸	内径（μm）	338	340
	膜厚（μm）	48	50
	空孔率（%）	78	75
平均ラメラ間距離（$\bar{\ell}_s$）（μm）	内表面部	—	1.38
	中央部	—	1.34
	外表面部	—	1.40
平均フィブリル束間距離（$\bar{d}_b$）（μm）	内表面部	—	0.49
	中央部	—	0.50
	外表面部	—	0.52
長円度（$\bar{\ell}_s/\bar{d}_b$）	内表面部	—	2.8
	中央部	—	2.7
	外表面部	—	2.7
標準粒子透過率SC（%）	0.08μm粒子	55	98
	0.20μm粒子	0	49
	0.33μm粒子	0	6.5
透水速度（ℓ/hr・m²・mmHg）		8.5*	14.8**
バブルポイント法最大孔径（μm）		0.41	0.63

Key: [translator's note: see original description for English, number and symbols]

Table 1

		Precursor	Porous Membrane
Hollow Fibers	Minor axis (μm)		
	Membrane thickness (μm)		
	Porosity (%		
Average distance $\bar{\ell}_s$ between lamella (μm)	Inner surface portion		
	Middle portion		
	Outer surface portion		
Average distance $\bar{d}_b$ between fibril bundles (μm)	Inner surface portion		
	Middle portion		
	Outer surface portion		
Ellipticity ($\bar{\ell}_s/\bar{d}_b$)	Inner surface portion		
	Middle portion		
	Outer surface portion		
Standard particle penetrability SC (%)	0.08 μm particles		
	0.20 μm particles		
	0.33 μm particles		
Water permeation rate (L/hr-m^2-mmHg)			
Maximum bubble point pore size (μm			

*The membrane was made hydrophilic with ethanol prior to the water permeation rate measurement.

**The water permeation rate measurement was performed by immersing the membrane directly in water without making it hydrophilic with ethanol.

(Working Example 2)

The hollow fiber spun at the same conditions as in Working Example 1 was used to obtain a precursor porous hollow fiber by changing only the temperature of hot drawing and drawing it at the same draw ratio conditions. Drawing was done under the same temperature at the 2nd and 3rd stages when the temperature at the 1st stage was reduced for the hot drawing temperature. The bundling and covering treatment was performed on the microfibrils with an ethylene/vinyl alcohol copolymer at the same conditions as in Practical Example 1. However, according to membrane Nos. 1 to 3, the time that the membrane was immersed in the copolymer solution was set to 10 minutes. Moreover, the porous hollow fiber membrane No. 5 was heat treated for 30 minutes under hot humid conditions at 120°C in an autoclave after drying the solvent. It was confirmed according to a scanning electron micrograph that all of the microfibrils of the resultant porous hollow fiber membrane were bundled, and that elliptical pores oriented in the longitudinal direction of the fibers were formed from these microfibril bundles and stacked lamella. The physical properties of each porous membrane are shown in Table 2.

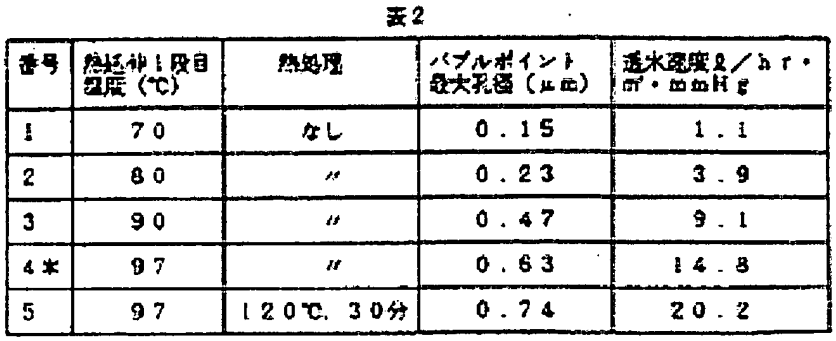

表2

番号	熱延伸1段目温度（℃）	熱処理	バブルポイント最大孔径（μm）	透水速度ℓ／hr・m²・mmHg
1	70	なし	0.15	1.1
2	80	〃	0.23	3.9
3	90	〃	0.47	9.1
4＊	97	〃	0.63	14.8
5	97	120℃, 30分	0.74	20.2

Key: [translator's note: see original description for English, number and symbols]

Table 2

No.	Temperature (6°C) at 1st Hot Drawing Stage	Heat Treatment	Maximum Bubble Point Pore size (μm)	Water Permeation Rate (L/hr-m^2-mmHg)
		N/A		
		120°C, 30 min.		

*Working Example 1 was reviewed.

(Practical Example 3)

A porous hollow fiber membrane was manufactured by using the same precursor as in Working Example 1 and using various linear polymers as the polymer for bundling the microfibrils. The concentration of each of these polymers was 1% by weight. Immersion was performed at room temperature and the immersion time was set to 10 minutes. The drying time was 1 hour. It was confirmed by observation with an electron microscope that the microfibrils of all the resultant porous membranes were bundled, and that elliptical pores were formed from these microfibril bundles and stacked lamella. The physical properties of each porous membrane are shown in Table 3.

表3

番号	線状高分子	溶剤	乾燥温度 ℃	透水速度※（ℓ／hr・m²・mmHg）	標準粒子（0.2 μm）透過率（%）
1	ポリスチレン	トルエン	70	11.5	41
2	ポリメチルメタクリレート	トルエン	70	12.3	37
3	エチレン−酢酸ビニル共重合体（酢酸ビニル含量67重量%）	酢酸エチル	50	10.9	43

Key: [translator's note: see original description for English, number and symbols]

Table 3

No.	Linear Polymer	Solvent	Drying Temperature °C	Water Permeation Rate (L/hr-m^2-mmHg)	Standard Particle (0.2 μm) Penetrability (%)
	Polystyrene	Toluene			
	Polymethyl methacrylate	Toluene			
	Ethylene/vinyl acetate (vinyl acetate content: 57% by weight)	Ethyl acetate			

*Measured after hydrophilized with ethanol.

(Advantages of the Invention)

The hollow fiber membrane of the present invention is a hollow fiber membrane wherein the ellipticity of the pores are lower and the manufacture thereof is easier than those of a known porous hollow fiber membrane, and moreover, the penetrability of high molecular weight components is improved substantially, and it is outstanding in safety.

4. Brief Description of the Drawings

Figure 1 is a scanning electron micrograph of the inner surface portion of the porous hollow fiber membrane obtained in Working Example 1 and Figure 2 is a scanning electron micrograph taken between the inner surface portion and outer surface portion of the porous hollow fiber membrane obtained in Working Example 1. Figure 3 is a scanning electron micrograph of the

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precursor hollow fiber membrane before being covered with the linear polymer in Working Example 1. Figure 4 is a transmission electron micrograph of a carbon vapor-deposited membrane slice.

Figure 1

才 1 図

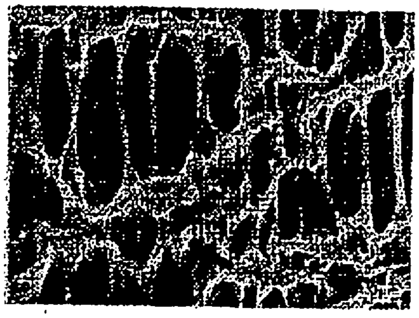
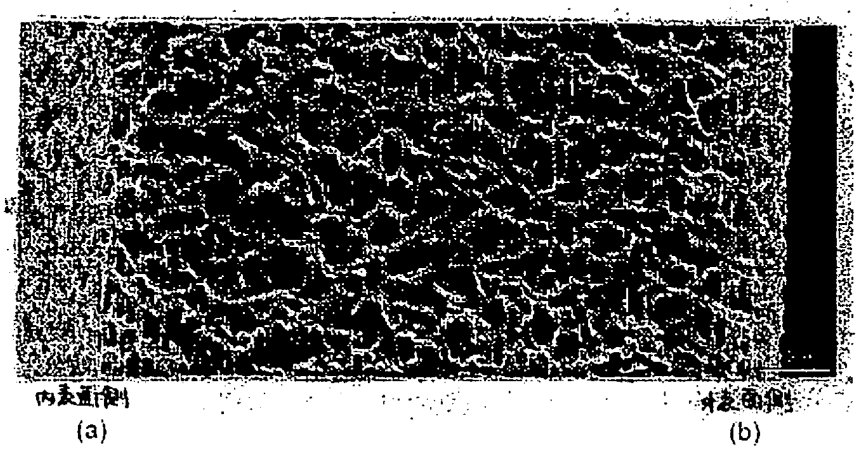


Figure 2

第2図



Key: (a) inner surface side; (b) outer surface side

Figure 3

第3図

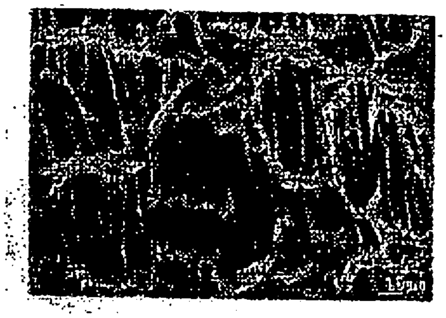


Figure 4

第4図